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A PROPOSAL FOR A RESEARCH PROGRAM ON FERRITES IN
THE MINERAL SCIENCES DIVISION OF THE MINES BRANCH

by

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MINES BRANCH
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Mineral Sciences Division Internal Report MS-65-98

A PROPOSAL FOR A RESEARCH PROGRAM ON FERRITES IN
THE MINERAL SCIENCES DIVISION OF THE MINES BRANCH

by

Norman F. H. Bright*, A. Hubert Webster** and Ian F. Wright***

SUMMARY

A proposal is outlined for initiating a program of research on ferrites in the Mines Branch. In the first instance, the program would be conducted almost exclusively in the Mineral Sciences Division and would be concerned with a study of the hexaferrite system, $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ - $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$ - $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$. Attempts would be made to prepare ferrites of compositions throughout this system by co-precipitation techniques, to fabricate them into ferrite shapes by ceramic procedures and then to test their magnetic properties. Studies would also be made of the crystallographic properties of compositions in this system. The work would later be extended to cover other possible compounds and compositions in the system $\text{BaO-SrO-PbO-Fe}_2\text{O}_3$. A study of the kinetics of ferrite formation may be made, as well as of the formation of oriented ferrites.

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Work on "soft" ferrites would be considered only when that on "hard" ferrites was complete. There is a possibility that raw materials for ferrites could be supplied from Canadian sources.

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INTRODUCTION

There has, of recent years, been an increasing interest in the subject of ferrites, or non-metallic magnetic materials fabricated into desired shapes by ceramic technological procedures. These materials are, in general, complex metallic oxide compounds of which ferric oxide, Fe_2O_3 , forms one component. The ferrites may be divided into two main classes:

- (a) "Hard" ferrites, which are permanent magnets and are often fabricated in such a way that they are oriented with the directions of magnetisation of the unit particles all aligned in approximately the same direction; the best-known hard ferrites are those based upon the stoichiometric formula $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$, where M is generally Ba with or without some degree of substitution by either Pb and/or Sr.
- (b) "Soft" ferrites, which become magnets only on the application of an external field and which rapidly lose their magnetic properties on removal of this field. Such materials are usually complex oxides, often having a spinel structure, of the general formula $\text{MO} \cdot \text{Fe}_2\text{O}_3$, where M can be Mg, Ni, Mn, Zn, Co or mixtures of almost any of these oxides.

Each of these two main types of ferrites has its own field of applications. The present situation of the technology of ferrites calls for a much greater demand for the "hard" materials, and it is mainly with such materials that the presently proposed Mines Branch program will be predominantly concerned in the first instance.

Since Canada is one of the world's main suppliers of iron oxide and since, also, there are, in Canada, large amounts of lead and significant deposits of strontium, for which there is at present relatively little demand, it is entirely reasonable that the Mines Branch should concern itself with such problems as ferrites, both by way of assistance to the primary production of the necessary mineral materials in the desirable state of purity, etc., and also by way of assistance to the secondary industries involved in the production and/or use of such ferrites. Indeed, there has recently been a substantial program of ad hoc work in the Mines Branch of precisely this type designed to provide assistance to a Canadian producer of high-grade natural and synthetic iron oxides, who wishes to provide materials for ferrite use (1)*. The presently proposed program, however, is not intended to be primarily an ad hoc investigation designed to benefit any particular manufacturer, but rather to be of more general benefit towards increasing the fundamental knowledge of these materials and towards providing a background of technological "know-how" on which any Canadian manufacturer of ferrites could rely. Hence, a program of work, admittedly of limited scope at present, has been devised and this present document is intended to give, in some detail, the considerations which will govern the precise fields to be studied and the directions along which effort will be exerted.

* For references, see pages 24 to 26.

During the past few years, much work has been done in the Mines Branch on the development of piezoelectric ceramic materials based upon the lead zirconate/titanate (PZT) solid-solution series. The main feature of this work has been the development of a co-precipitation technique for the preparation of the compositions on which these materials are based in order to give an adequate control of stoichiometry and enhanced sintering behaviour. Many of the same techniques developed in connection with this work are considered to have a probable application also in the ferrite field and, hence, much of the equipment employed and many of the procedures used will probably bear much similarity to those involved in the PZT work. The PZT work has been supported by contracts between the Mines Branch and the Defence Research Board for research work on Electronic Ceramics in general. It is considered that the magnetic ceramic materials that form the subject of the present program lie within the scope of the general term "Electronic Ceramics" and support for the ferrite work will also come under the heading of these same contracts.

INITIATION OF THE MINES BRANCH PROGRAM

On June 14, 1965, a meeting was held of various people who probably will be involved to a greater or less extent in the proposed program, for the purpose of deciding on which precise aspects of the work our effort should properly be placed and who would actually be involved in the consequent experimental work. The Minutes of this meeting are given as an Appendix to this report.

It will be seen from these minutes that the immediate objective of the program is a study of the system $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ - $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$ - $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$. There is a considerable amount of information currently available on the compounds of this three-component system, particularly on the first two compounds. It will be necessary to review this work and to determine what, if anything, needs to be done on the end-members in the first place, and secondly, on the bounding binary systems before proceeding to work dealing with the inside of the ternary system. The intention is to study this system from four standpoints:

1. Chemical - by preparation of various compositions of one, two or three components, preferably by a co-precipitation type of procedure; it will be necessary to demonstrate that the stoichiometry can be controlled within the desired limits by such a procedure. Special methods of analysis for verification of stoichiometry may be necessary.
2. Ceramic - the co-precipitated "ferrite" powders will, in the first stages of preparation be in the form of mixed oxides, hydroxides, carbonates, oxalates or some other convenient compound. Calcination conditions for the formation of the ferrite compound will have to be determined. It is likely that the techniques of differential thermal and thermogravimetric analysis will prove useful at this stage. The conditions of pressing and sintering to form a ceramic

body will then have to be determined. Temperature and atmosphere control are probable complications at this stage. If, as has been indicated earlier, it becomes desirable to fabricate ferrites with an oriented direction of magnetisation, then additional complications at the pressing stage will be introduced, since, presumably, it will be necessary to subject a slurry of ferrite precipitate to an intense magnetic flux before de-watering and pressing prior to the sintering stage. This matter is discussed in greater detail later in this report.

3. Crystallographic - If, in fact, the three end-member compounds can be shown to exist, it will be necessary to demonstrate whether or not they have the same crystal structure, and hence, whether two- and three-component solid-solution series are to be expected. Assuming that such exist, it will be desirable to follow the variation of the hexagonal unit-cell parameters of the hexaferrite series over the whole three-component system. It may be possible to use these parameters as a diagnostic indication of composition. Another crystallographic aspect of the problem that should be followed up is the construction of an atomic crystal model of the hexaferrite lattice in order to correlate the magnetic with the crystallographic properties and to investigate the possible location(s) for substituent

or "doping" atoms.

4. Magnetic - The magnetic properties of the whole range of hexaferrite compositions should be surveyed with the object of preparing a "contour" map of these parameters. It should then be possible to delineate an optimum composition. Still further improvement in the magnetic properties may then be obtained by doping this optimum composition with minor amounts of one or more additives

In the event that no complete solid-solution series exists between these various hexaferrites, then consideration will have to be given to the other compounds that can be formed between PbO, SrO, and/or BaO and ferric oxide and to the existence of other solid-solution series that may be formed in the quaternary system PbO-BaO-SrO-Fe₂O₃. Again, a survey of the relevant chemical, ceramic, crystallographic and magnetic properties will be necessary. In fact, such a study may be desirable even if a complete hexaferrite series is demonstrated to exist.

It is known that much work has been published on many aspects of ferrite compositions and care should be taken to avoid any unnecessary duplication of effort. It must, however, be borne in mind that materials of controlled stoichiometry prepared by a co-precipitation type of procedure often vary substantially in properties, particularly in ceramic behaviour, from materials fabricated directly from mechanically mixed oxide compositions.

PERSONNEL AND ADMINISTRATIVE CONSIDERATIONS

The two Sections in the Mines Branch that will be most heavily committed in this proposed program are both in the Mineral Sciences Division; indeed, certainly in the early stages of the investigation, there is not likely to be any substantial involvement of any group outside this Division. The chemical, ceramic and crystallographic aspects of the work will be done in the Physical Chemistry Section as follows:

Chemical Work - Dr. Sutarno, with the general surveillance by
Dr. A. H. Webster.

Ceramic Work - Dr. Sutarno, with the general surveillance by
Dr. A. H. Webster.

Crystallographic Work - Mr. J. F. Rowland.

The magnetic testing and any advice on specialized equipment, perhaps for oriented ferrite preparation, will be done in the Mineral Physics Section by Mr. J. L. Horwood and Mr. G. E. Alexander.

The Analytical Chemistry Sub-division will probably be involved to a substantial degree in the provision of accurate analyses as a control on the stoichiometry of the co-precipitated products.

In view of his continuing interest in this work, his contacts with the relevant interested industries and his liaison with the Defence Research Board etc., it was felt that Mr. I. F. Wright, of the Mineral Processing Division, would be the most appropriate person to act as the co-ordinator of the administrative aspects of the whole project.

It is probable that, in the co-precipitation work, the co-operation of the Extraction Metallurgy Division may be desirable in the loan of certain equipment assembled by them in the earlier stages of the PZT work. Similarly, the assistance of the Naval Services Section may be required in lapping of sintered shapes, preparatory to magnetic testing.

OTHER POSSIBLE LINES OF INVESTIGATION

Several months before the program, as outlined on the preceding pages, was formulated, some consideration was given to other aspects of the physical chemistry of ferrite formation that might merit investigation in the Mines Branch. Although a somewhat different program has now been adopted as our primary aim, namely the phase equilibrium, crystallographic and magnetic study of the hexaferrite systems, it is thought worth while to place on record the thinking as to the possible course of the program at that earlier date. It is quite possible that some of the considerations and lines of study proposed at that time might find application in the program presently devised. The programs considered as of the earlier date were concerned primarily with three aspects of barium ferrite technology:

- (a) The kinetics of ferrite formation;
- (b) The fabrication of oriented $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$;
- (c) The effects of impurities on the magnetic properties of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$.

It will be seen that items (b) and (c) also find a place in the present program and that it may be necessary to take into account some of the factors involved in the discussion of item (a) when dealing with the hexaferrite system in the proposed manner. These three aspects of possible work on hard ferrites will be discussed in turn.

THE KINETICS OF THE FORMATION OF FERRITES

A. Some Previous Studies

1. Barium Ferrite, $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ or $\text{BaFe}_{12}\text{O}_{19}$.

Studies conducted in the Mineral Processing Division of the Mines Branch a few years ago by Sadler (2a, b, c, d)* indicated that, in the reaction between barium carbonate and ferric oxide, barium oxide or, more probably, BaO containing a certain proportion of iron substitution, is formed as the only detectable intermediate compound during the formation of the ultimate product, barium ferrite, $\text{BaFe}_{12}\text{O}_{19}$. This finding is in agreement with the results reported by Erchak, Frankuchen and Ward (3). The formation of BaO was observed by Sadler at temperatures between 650°C and 850°C, and by Erchak et al. between 500°C and 950°C. These latter workers also reported the formation of an additional intermediate product which they postulated to be $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$; however, Sadler attributed the X-ray diffractions on which this identification was based to barium peroxide BaO_2 . Suchet (4), on the other hand, has reported the formation of BaFe_2O_4 as an intermediate compound. The initial temperature of

the formation of $\text{BaFe}_{12}\text{O}_{19}$ has been variously reported as being 730°C (3), 750°C (2) and 820°C (4).

The rate of reaction between barium carbonate and ferric oxide has been studied by Sadler by following the isothermal weight loss due to the evolution of CO_2 . The results obtained were then treated on the basis of Jander's equation for the decomposition of solid materials to yield solid and gaseous products, viz:

$$Kt = \left[1 - \sqrt[3]{1 - \frac{x}{100}} \right]^2 \text{-----} (\text{Eq 1})$$

where K = a constant,

t = time

and x = fraction of material reacted (in percentage).

Deviations from Jander's relationship were observed for large values of x at temperatures above 750°C . An apparent activation energy of the decomposition process of 45.5 Kcal/mol was found for temperatures below 730°C , whereas, for temperatures above this figure, a value of 73.2 Kcal/mol was obtained, indicating some difference in the mechanism of the reaction above and below this particular temperature. Sadler postulated the formation of a product layer on the reactant which could act as a barrier to any diffusing species.

It should, however, be noted that the rate of evolution of CO_2 , as given by the weight loss, indicates merely the decomposition of the barium carbonate and is not, of itself, any measure of the rate of

formation of the ferrite, $\text{BaFe}_{12}\text{O}_{19}$.

2. Nickel Ferrite, NiFe_2O_4

The reaction between NiO and Fe_2O_3 , using Fe_2O_3 of five different particle sizes with a fixed particle size of NiO , was studied by Economos and Clevenger (5). Their results were also interpreted using the Jander equation. An apparent activation for the combination process between NiO and Fe_2O_3 to give NiFe_2O_4 of about 56 ± 2 Kcal/mol was found for all Fe_2O_3 samples except one anomalous material that gave an apparent activation energy of 70 Kcal/mol. There did not appear to be any good correlation between the reaction rate and the particle size of the Fe_2O_3 used.

Economos (6) compared the reactivities of the following mixtures: ($\text{NiO} + \text{Fe}_2\text{O}_3$), ($\text{NiCO}_3 + \text{Fe}_2\text{O}_3$), mixed hydroxide precipitates and a mixed oxalate precipitate having the formula $\text{NiFe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$. The oxalate and hydroxide precipitates were found to form ferrites much more readily than the mixed powdered materials. The mixed hydroxide precipitate was formed using tetramethyl ammonium hydroxide as the precipitating agent.

3. Magnesioferrite, MgFe_2O_4

Fresh (7) followed the reaction between MgO and Fe_2O_3 by means of quantitative X-ray diffraction examination of samples reacted for a range of times at a series of temperatures. Various

particle sizes of MgO and of Fe_2O_3 were used and the results, again, were treated using Jander's equation. When both fine MgO (0.03 micron) and fine Fe_2O_3 (0.05 micron) were used, an activation energy of 27 Kcal/mol was claimed (8). When either coarse MgO or coarse Fe_2O_3 were used along with a finely-divided second reactant, higher activation energies were found.

B. Study of the Reaction Between

BaCO_3 and Fe_2O_3

1. Purposes of the Study

The principal purposes of this portion of the program would be:

- (a) to determine the effect of the particle size of the Fe_2O_3 on the reaction rate;
- (b) to determine, if possible, the nature of the diffusing species.

2. Materials to be Used

- (a) Barium Carbonate - This should be a good, reagent-grade material. Its particle size should be determined by microscopical examination (either optical or electron, as required); the impurities present should be determined by spectrographic analysis.

Note: Barium chloride could conceivably be used as an alternative source of barium, particularly if any co-precipitation work is to be conducted, and thus would probably be the starting material in the program on the hexaferrite system.

- (b) Ferric Oxide- This could be prepared by precipitating ferrous oxalate from ferrous ammonium sulphate with oxalic acid. The oxalate can be conveniently converted into Fe_2O_3 by ignition in air. The use of various calcination temperatures should yield a range of particle sizes. Test ignitions should be done first at various temperatures, with the particle sizes being determined by either optical or electron microscopy. If the ranges of particle size within any given sample are too great for convenience, the samples could be fractionated by a sedimentation procedure. The Fe_2O_3 should also be checked for impurities by spectrographic analysis. It is considered that at least four different particle sizes should be employed, ranging from 0.5 micron or less to 30 microns or more. At least 80 g of each particle size of material would probably be necessary for the investigation.

It is probable that materials prepared by such a precipitation technique will have substantially lower bulk densities than that of natural material. Determinations of specific surface area of the samples should be made using a sorptometer or other suitable equipment. Such an instrument has now become available in the Mineral Processing Division.

- (c) Special Techniques- The possibility of making mixed barium

and iron oxides by co-precipitation will certainly be looked into in order to provide materials of standard purity and stoichiometry in connection with the newly-devised hexaferrite program.

It may also be profitable to investigate the possibility of preparing "ultimate mixtures" of BaO and Fe_2O_3 by the Flaschen process (Comment by Mr. I. F. Wright).

The use of hydrothermal procedures for single-crystal ferrite preparation may also merit study.

3. Rate Studies

Since, as has been mentioned, the rate of decomposition of BaCO_3 does not necessarily indicate the rate of formation of $\text{BaFe}_{12}\text{O}_{19}$, studies that include only the determination of weight loss with time will not give as much information as would be desirable. It is suggested that a combination of methods could be tried and that the most suitable be selected for more extensive investigation. Such methods include:

- (a) Quantitative X-ray Diffraction of the Products- The products (intermediate and final) that have been reported, i.e., BaO, $\text{BaFe}_{12}\text{O}_{19}$ and possibly, $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$ or $\text{BaO} \cdot 4\text{Fe}_2\text{O}_3$, should be confirmed and quantitative estimations should be made of them on the basis of prepared standards. This method of analysis is known to have certain pitfalls since $\text{BaFe}_{12}\text{O}_{19}$ is highly anisotropic and, hence, may give preferred orientation effects during the preparation of the specimens for X-ray diffractometry.
- (b) Differential Thermal Analysis-The possibility of studying

the reaction by differential thermal analysis (DTA) has been suggested. This could be done on mechanically-mixed oxides and on co-precipitated materials, when such have been made. The form and area under the various DTA peaks could well give some information as to the relative reactivity of the various specimens.

- (c) BaCO₃ Decomposition by Weight Loss- This can be studied by thermogravimetric analysis (TGA). The reaction products could be leached with a dilute or a weak acid (e.g., acetic acid) to remove residual BaCO₃ and also BaO, if this is indeed an intermediate product, and, in addition, any other soluble intermediate products. The quantity of barium in the leach solution could be determined. From this quantity, the amount of barium that has reacted to form the insoluble final product, BaFe₁₂O₁₉, could be calculated. Examination of the leach residue by X-ray diffraction should also be conducted on some samples to verify the validity of the leaching process as a means for studying the reaction. The rate of acid attack on BaFe₁₂O₁₉ should be checked in separate experiments. It may also be necessary to determine Fe in the leach solution if a soluble iron-containing intermediate product is encountered.

Preliminary experiments could be done to determine if:

- (i) the rate of reaction depends on whether the mixed powder is in the loose or pressed form; pressed powders are suggested for routine work as being more readily controllable;
- (ii) the procedure of mixing the powders in a mechanically-driven agate mortar is sufficient; various mixing times should be tested. With co-precipitated materials, no mixing may be needed.

The rate of reaction should be determined for about six temperatures within the range 650° to 950°C and for each of the four particle sizes of Fe_2O_3 . Samples would be prepared for withdrawal from the reaction temperature at six different times in each experiment, the times of withdrawal being governed by the reaction temperature. The sample pellets, held in a suitable container (Pt crucibles?), would be inserted into the reaction furnace at temperature and would be quenched on withdrawal from the furnace.

Microscopical examinations should be made of all products containing any substantial proportion of $\text{BaFe}_{12}\text{O}_{19}$ in an attempt to determine the crystallite size of this compound. This figure will be of considerable interest with respect to the fabrication of oriented polycrystalline $\text{BaFe}_{12}\text{O}_{19}$ specimens. (See pages 20 to 22.)

A similar rate study could be conducted using Fe_2O_3 sample(s) by industrial organizations. Where such samples of representative Fe_2O_3 are obtained from such a source, the following work should be conducted with them, in addition to the above-mentioned rate studies:

- (i) They should be characterized as to surface area, particle size, particle shape and chemical composition as far as possible:
- (ii) Various particle size fractions should be obtained, either by sedimentation or by a rolls analyser (which will cut down to a 3μ size):
- (iii) Intimate mixtures of the Fe_2O_3 with BaCO_3 could possibly be obtained by stirring the Fe_2O_3 in a BaCl_2 solution and, by means of either CO_2 or ammonium carbonate, precipitating the BaCO_3 on Fe_2O_3 nuclei; if segregation occurs, then freeze-drying could be employed to assist in mixing. (N.B. These three procedures, (i), (ii) and (iii) above, were suggested by Mr. I. F. Wright).

The work already done on iron oxides, both natural and synthetic, from a particular manufacturer (1), will be distinctly relevant in this connection.

4. Intermediate Products

Barium oxide, BaO , has been reported as being formed in the presence of Fe_2O_3 at temperatures much lower than that at which BaCO_3 alone will decompose. (This is by no means an uncommon form of behaviour e.g., $\text{CaCO}_3 + \text{SiO}_2$ yields calcium silicates at temperatures well below the CaCO_3 decomposition temperature). This behaviour raised the question as to whether there is any kind of association formed between the BaO and Fe_2O_3 e.g., solid solution. Sadler's results (Reference 2(b), Table 7 and Figure 8) indicate that, at 700°C and at 750°C , the proportion of Fe_2O_3 in the reaction mixture decreases as the BaCO_3 decomposes, even though no detectable amount of $\text{BaFe}_{12}\text{O}_{19}$ has been formed. The results of Erchak et al. (3) indicate that the greatest yield of "BaO" (i.e., BaO with possible Fe_2O_3 association) is obtained from a mixture containing about 50 wt. % of BaCO_3 at 750°C .

It is possible that the question of "BaO" formation could be clarified by leaching a reaction product with a weak acid that would attack the BaO (as such) but would have little effect on Fe_2O_3 . If the "BaO" were not soluble, then it would indicate quite strongly that this phase was not free pure barium oxide. If, however, the phase were soluble, then Fe_2O_3 could be determined in the leach solution and an estimate of the iron content of the "BaO" phase could be obtained thereby. The leaching process should also be monitored by X-ray diffraction examination of the leach residues.

5. Studies of Reactions Between Compressed Pellets

Experiments with mixed powder samples do not, in general, yield any indication as to the nature of the diffusing species. On the other hand, this can sometimes be determined from studies of the products found at the interface between composite macroscopic pellets. Studies of the formation of spinels from $(\text{MgO} + \text{Al}_2\text{O}_3)$ and from $(\text{MgO} + \text{Fe}_2\text{O}_3)$ have been made using this technique by Carter ⁽⁹⁾. Often, inert markers of such material as platinum wire are used to indicate the position of the original interface, but Carter reports that, in the presence of iron, such markers were destroyed. However, he found that the original pore distribution in the pellets was preserved during sintering and reaction, and thus could be used as a marker for the location of the reaction interface.

In the present problems, pellets of Fe_2O_3 and BaCO_3 alone could be sintered in oxygen and in CO_2 , respectively. The resulting single-component pellets could then be firmly held together and maintained at various reaction temperatures (possibly 6 hours at 700°C , 800°C and 900°C could be tried initially). Platinum wire markers could possibly be tried, but success

with such markers is, at the very least, doubtful. Scribing small grooves on the contact surface of one or other of the pellets might possibly be used to form a "void" marker; the location of the product layers or reaction interface could then be determined by microscopical examination; such studies should indicate which species has undergone diffusion. The electron microprobe analyser could very probably prove a useful tool in this work.

It should be noted that, in accordance with the previously mentioned earlier studies, it is probable that other products than merely $\text{BaFe}_{12}\text{O}_{19}$ could be expected. It may be possible to identify the location of the $\text{BaFe}_{12}\text{O}_{19}$ by making use of its magnetic properties; if the polished surface is sprinkled with very-finely-divided iron-metal powder, the distribution which this material takes up should indicate the distribution of the $\text{BaFe}_{12}\text{O}_{19}$.

6. Other Studies on Reactions Between Oxides

A paper entitled "Thermal Stability of Barium Ferrite", ($\text{BaFe}_{12}\text{O}_{19}$) by H.J. van Hook of the Raytheon Company ⁽¹³⁾ that deals with some of the thermodynamic aspects of the system $\text{BaO-FeO-Fe}_2\text{O}_3$ over a range of temperatures and oxygen pressures is relevant and its implications should be considered in connection with the hexaferrite work.

Quite extensive studies of the reactions between MgO and Fe_2O_3 and between NiO and Fe_2O_3 have been made, including studies of the effect of particle size. Hence, studies on these systems at the

Mines Branch are not suggested at present. Other systems should not be attempted until the work suggested on barium ferrite, $\text{BaFe}_{12}\text{O}_{19}$ and the other hexaferrites has been completed.

THE FABRICATION OF ORIENTED $\text{BaFe}_{12}\text{O}_{19}$

(N.B. This material is marketed under the trade name of "Ferroxdure" for use in permanent magnets.)

Barium ferrite, $\text{BaFe}_{12}\text{O}_{19}$, has a hexagonal structure and exhibits marked magnetic anisotropy, with the hexagonal axis being the direction of easy magnetization. The crystal habit of $\text{BaFe}_{12}\text{O}_{19}$ is a platelet form, with the hexagonal axis perpendicular to the face of the platelet. In order to achieve the maximum residual magnetization in the polycrystalline material, the hexagonal axes of the platelet-like grains should all be oriented in one direction. The degree of orientation of the platelets can be indicated by the ratio $B_{r\perp} : B_{r\parallel}$, where $B_{r\perp}$ = residual inductance perpendicular to the desired direction of the hexagonal axes and $B_{r\parallel}$ = residual inductance parallel to the desired direction of the hexagonal axes; this ratio should be small for a well-oriented material.

The grain size of the $\text{BaFe}_{12}\text{O}_{19}$ ceramic body must be kept down to about 1 micron or less, otherwise the coercive field, H_c , will decrease due to the movement of the Block wall between the domains. Below a certain critical size (about 1 micron for $\text{BaFe}_{12}\text{O}_{19}$), only one

domain per grain can exist. For good permanent magnet material, a high value of $(BH)_{\max}$ is required. In addition, the electrical resistivity of the material should be high.

The powder for pressing to produce oriented permanent magnets should preferably consist of single-crystal particles having a 1 micron or less grain size. This is generally achieved by grinding to a $<1 \mu$ particle size but might be achieved directly by a co-precipitation procedure. The resulting powder is then placed in a die and the particles oriented by the sudden application of a field of the order of 11,000 oersted. The particle alignment thus achieved is then stabilized by pressing and the piece so formed is sintered under controlled conditions of time and temperature to give a ceramic body of good density without excessive grain growth. The oriented particles are found to grow at the expense of the un-oriented ones during the sintering process.

In order to fabricate oriented ferrites, a die such as that described by Stuijts et al. ⁽¹⁰⁾ will be required. A sketch of the die, showing its essential features is given as Figure 1.

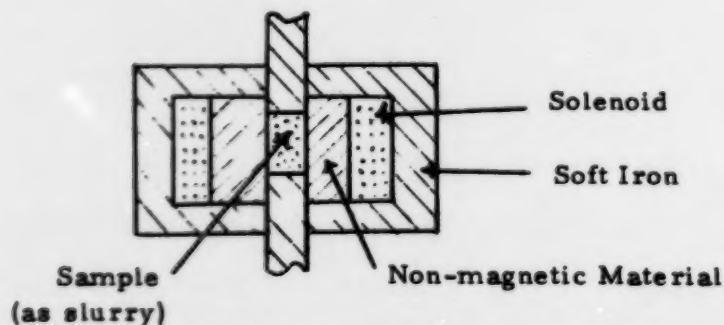


Figure 1 - Die for Fabrication of Oriented Ferrites

An estimated 10,000 ampere-turns should give somewhat more than the required field for a 1-inch air gap between the plungers of such a die. The non-magnetic material indicated in Figure 1 could be an austenitic stainless steel. Various power inputs to the solenoid would have to be tried in order to determine the optimum conditions for orienting the ferrite powder. A series of experiments would also be necessary to determine suitable sintering conditions to yield a ceramic of high density without undue grain growth. The preferred procedure for making the starting material, the barium ferrite powder, would be determined from the results obtained in the hexaferrite studies.

The samples made using the above procedure would be in the form of cylinders with their direction of easy magnetization along the cylinder axis. The B-H curves for this direction could be determined by a "yoke" method, as described by Brockman and Steneck⁽¹²⁾, or by a modification of this method. Electrical conductivities of such materials should be high enough to be determined by a two-probe method using a megohm-meter in contact with electrodes of conducting silver paint applied to the ends of the cylinder. Polished sections of the cylinders should be examined to determine the grain size and orientation of the material.

It should be noted that, if the method of Brockman and Steneck is to be used for the B-H loop determinations, the equipment, including an electromagnet capable of producing a homogeneous field of about 4,000 oersted, integrating circuits and an X-Y recorder, will be

required.

It should also be noted that it is doubtful if a solenoid of the size indicated in Figure 1 could be fitted into the space available in the ARL hydraulic press available in the Physical Chemistry Section; hence, a larger press may be necessary; it is possible that such a press is currently available.

EFFECTS OF IMPURITIES ON THE MAGNETIC

PROPERTIES OF $\text{BaFe}_{12}\text{O}_{19}$

Once the method of fabricating and testing oriented $\text{BaFe}_{12}\text{O}_{19}$ and other hexaferrite samples has been satisfactorily developed, the effects of impurities added to either the BaCO_3 , Fe_2O_3 or other starting materials should be examined. It is suggested that the incorporation of SiO_2 , Al_2O_3 , or MgCO_3 at the 0.05%, 0.1% and 0.5% levels would indicate the effects of impurities that might possibly be present as gangue in either the BaCO_3 or Fe_2O_3 derived from a high-grade iron ore. The effect of the presence of sulphate should be examined as this is a possible contaminant in Fe_2O_3 formed by precipitation. Commercial organizations could be called upon to provide Fe_2O_3 samples of known levels of impurity for examination.

FURTHER WORK

All the foregoing covers only investigations of ferrites for permanent magnets (i.e., "hard" ferrites). Investigations of "soft"

magnetic materials could be considered at a later date and will be made the subject of a separate program summary at that time.

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(N.B More recent work by Sadler et al. has appeared in the Journal of the Canadian Ceramic Society, 1964).

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APPENDIX

MINERAL SCIENCES DIVISION

June 14th, 1965

1.30 p. m.

Meeting Re: PROPOSED FERRITE PROGRAM

PRESENT Dr. A.T. Prince, Chief, Mineral Sciences Division
Dr. J.D. Keys, Head, Mineral Physics Section
Dr. N.F.H. Bright, Head, Physical Chemistry Section
Dr. A.H. Webster, Physical Chemistry Section
Dr. Sutarno, Physical Chemistry Section
Mr. J. L. Horwood, Mineral Physics Section
Mr. G. E. Alexander, Mineral Physics Section
with
Mr. I. F. Wright, Mineral Processing Division
(Co-ordinator of Electronic Ceramics Program)

INTRODUCTION

Research on ferrites or magnetic ceramics is provided for within the contract between Mines Branch and the Defence Research Board for research on Electronic Ceramics in general.

Several government supported projects on ferrites exist in Canada, but none of the contractors are as well equipped or qualified for this work as the Mines Branch, particularly in the area of basic research. Mines Branch provided technical consultants for these projects and, in order to discharge these duties adequately and provide a certain amount of leadership and assistance to new secondary industries, should undertake research in the more difficult areas not only to obtain basic information, but to provide back up for the technical consultant as well.

Several Canadian companies are interested in supplying various oxides for the electronic ceramic industry; the application most likely to require the largest tonnage is in the manufacture of hard ferrites.

Hard ferrites are largely made from powdered $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ with some substitution of PbO and SrO for BaO . A great deal of uncertainty exists concerning the formation and stability of compounds of this composition and it was decided that a study of structural and magnetic properties of phases existing in the ternary system of Ba , Pb and Sr hexaferrites would make a useful contribution to existing knowledge.

Such a study would not only fall well within the terms of reference of the Mineral Sciences Division, but could lead to the creation of new markets for present Canadian supplies of PbO and provide an incentive for the development of Canadian strontium deposits.

A future study of the quaternary system from $\text{MO} \cdot \text{Fe}_2\text{O}_3$ to $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ (where $\text{MO} = \text{BaO}$, PbO or SrO) might also prove interesting for other applications.

PERSONNEL COMMITMENT

The Division's present commitment to the overall program, and current status of the work were reviewed, and it appeared that Dr. Webster's active participation would be required for at least another year. Dr. Webster agreed that many of the operations had become routine and could be performed by a technician. Dr. Bright stated that an increase in technician strength would not be necessary and that technician assistance could be provided by a more economical use of existing staff.

Dr. Webster stated that there would be no advantage in Dr. Sutarno's participation in the P.Z.T. program in the immediate future and that it would be preferable for Dr. Sutarno to give his full time to the ferrite program.

Dr. Sutarno stated, for initial requirements for precipitates, volumes of solutions would be small enough to be handled on a bench scale, and that there would be no necessity to request assistance from other divisions for powder preparation at this time.

Mr. Horwood and Mr. Alexander stated that more equipment would be required for testing hard ferrites. Dr. Keys stated, however, that the balance of the equipment necessary was on order. Mr. Horwood and Mr. Alexander will be available for advice on the construction of equipment for making oriented ferrites as well as testing them.

Mr. Wright will act as co-ordinator of the project.

Ian F. Wright